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BRILLOUIN, RAYLEIGH AND RAMAN SCATTERING OF LASER LIGHT FROM LI--ETC(U)
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Contract # N00014-75-C-0908

(15)

(9) (6) FINAL TECHNICAL REPORT.

Brillouin, Rayleigh and Raman Scattering of

Laser Light from Liquid Crystals and Polymers .

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(11) December 1978

(12) 15 p.

400 730

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I. Project Goals

For the investigation of intermolecular interactions and dynamics of motion of polymer segments and whole polymer molecules in solution and in bulk, we originally proposed detailed experimental and theoretical studies of:

1) Brillouin scattering spectra of bulk polymers and structural relaxation in bulk polymers.

2) Depolarized Rayleigh scattering spectra of polymer solution as a function of temperature and composition.

3) Raman scattering spectra of chain orientation in solid polymers. and

4) Structural relaxation in polymer liquids and solution using photon correlation and light beating spectroscopy.

Substantial progress has been made on categories 1), 2) and 3) above. The equipment for category 4) has only just been set up.

Apart from successful completion of most of the original proposed goals, we have also developed a generalized hydrodynamic model for describing the effect of sctructural reláxation on the Rayleigh-Brilouin spectra of bulk polymers and polymer solutions to interpret the experimentally observed hypersonic frequency, attenuation coefficient and the Rayleigh-Brillouin intensity ratio of polymer liquids.

II. Summary of Accomplishments

We organize our discussion into categories of Section I above. Thirteen published papers[1-13], two yet-to-be published papers[14,15] and various unpublished results are here summarized. The thirteen publications on polymers have been distributed as technical reports, remaining publications will be distributed as technical reports when available in final form.

1) **Rayleigh-Brillouin Scattering Spectra of Bulk Polymers.**

   a) **Brillouin and Rayleigh Scattering in Polybutadiene:** Measurements of hypersonic frequency, Brillouin spectral linewidth and Rayleigh depolarization ratios of polybutadiene were made as a function of temperature ranging from 110 to 350 K. The hypersonic attenuation coefficient over one hypersonic wavelength was found to be insensitive to temperature variation below the glass transition temperature (T_g). Above T_g, the attenuation coefficient increases rapidly with increasing temperature. The theory of Woodruff and Eihsenreich which describes the sound attenuation in terms of the rate of energy transfer of thermal phonons to the temperature bath gives an adequate description of the sound attenuation of polybutadiene below T_g; however, no quantitative theory describes the phenomena above T_g. The Krishnan effect was observed for this system below 250 K, and the frozen-in fluctuations of dielectric anisotropy are proposed to be a possible mechanism for the observed effect[1].

   b) **Brillouin Scattering Studies of Polypropylene Glycol:** A comprehensive Brillouin scattering study of polypropylene glycol[2,3,4], having molecular weight 425, 1025, 2025 and 4000 was carried out. The hypersonic velocity, attenuation coefficient, the modulas of elasticity and the Landau-Placzek ratio have been obtained as a function of temperature for each polymer of a well defined molecular weight. For all quantities measured, only the Landau-Placzek ratio below ambient temperature is found molecular dependent, the hypersonic velocity, attenuation coefficient, and elastic modulus are independent of molecular weight in the 425-4000 range. All polymers display considerable velocity dis-

persion and a maximum in the sound attenuation versus temperature curve. However, contrary to that observed in the ultrasonic frequency region, the maximum of the hypersonic attenuation coefficient appears to lie close to the beginning of the velocity dispersion curve and not at the middle. Before we developed our generalized hydrodynamic theory to interpret this phenomena we employed the Isakovich-Chaban theory to fit the experimental results. The fit was found in qualitative agreement with the experimental result at low temperature only.

c) Comparison of Dielectric Relaxation and Brillouin Scattering Results in the Study of Molecular Relaxation of Polypropylene Glycol Solution: To elucidate the mechanism responsible for the molecular relaxation of polypropylene glycol, dielectric relaxation and Brillouin scattering techniques were jointly used for the study of the polypropylene glycol-methylcyclohexane binary system. The dielectric method was applied to more concentrated solutions (100%, 80%, 60%, by volume) over a wide temperature and frequency range. This enables us to delineate the variation in activation energy characteristic of a glass-forming substance. This work also extends previous work on the undiluted polymer to higher frequencies so that a total range of 12 decades in the dielectric loss maximum as a function of temperature is now available. The "Antoine" equation is found to represent the behavior of log f_{max} of the bulk concentrated solutions rather well. The more dilute (40%, 20%) solutions were studied only in the high frequency (GHz) region since phase separation occurred at low temperature. Brillouin scattering spectra were obtained at several scattering angles

and a wide range of temperatures. A maximum in the hypersonic attenuation versus temperature was observed in each polymer solution. The attenuation maximum shifts toward lower temperature upon dilution, in agreement with the dielectric relaxation result. However, the Brillouin scattering result follows different activation parameters and evidences a more rapid process than does the dielectric relaxation. It is speculated that it monitors a secondary or subglass relaxation, due perhaps to damped torsional oscillations[5]

d) Brillouin Scattering of Bulk Polymers and the Proposition of a Generalized Hydrodynamic Theory: After the Brillouin spectra of the polypropylene glycol samples have been carefully studied, a clear picture about the underlying physical process for the viscous bulk polymer liquid starts to emerge. It is believed that for polymer liquids of high viscosity, Brillouin scattering is closely associated with the structural relaxation due to segmental motion of the polymer chain. The torsional motion involving a small number of monomeric units is probably responsible for the dispersion and attenuation of the hypersonic wave. This explains why the Brillouin scattering spectrum of a polymer liquid is insensitive to change of molecular weight.

To obtain more experimental results to support this observation, the Brillouin spectra of oligomers of polyethylene glycol, along with ethylene glycol, were studied[6]. Again similar to the result of polypropylene glycols, it was found that with the exception of ethylene glycol the Brillouin frequencies and linewidths of the oligomers of polyethylene glycol are independent of viscosity and molecular weight. All of the experimental results now available

indicate that the motion responsible for the hypersonic wave dispersion and attenuation is localized, and there is a need for developing a new theory to account for this result.

Starting from the first principle, we have employed linear response theory using a complete set of dynamic variables involving density, velocity and energy fluctuations to analyze the Brillouin spectrum of a viscoelastic polymer liquid[8,9]. An exact equation including the effect of structural relaxation has been derived and incorporated in the generalized hydrodynamic theory. The evolution of structural relaxation and its effect on the entire Rayleigh-Brillouin spectrum is described. The structural relaxation gives rise to a new central peak which is most pronounced where the frequency dispersion and the linewidth maximum are present. The theoretical result fits well to the observed Brillouin spectra of polypropylene glycols, polyethylene glycols and other polymeric liquids[14], and it is believed that this theory will serve to guide the experimentalists in unravelling the complex physical processes associated with Brillouin scattering of polymer liquids.

2) Depolarized Rayleigh Scattering of Polymer Solutions.

To corroborate the finding in Brillouin scattering, the depolarized Rayleigh scattering spectra of polypropylene glycol in optically isotropic cyclohexane solvent were studied as a function of temperature, molecular weight and concentration. By studying the dependence of relaxation times on viscosity, temperature and concentration and also comparing the results with the theoretical predictions of molecular and side group reorientations, the depolarized Rayleigh scattering spectra of polyperopylene glycol are found to be associated with the

segmental motion of polymer backbone[9]. At the same viscosity over temperature ratio the relaxation times for dilute solutions were found to be larger than those of concentrated solution, thus suggesting the importance of the pair angular correlation effect in concentrated solutions. The Rayleigh relaxation times were also found to be independent of the molecular weight of the polymer. This result establishes without a doubt that the mechanism for the depolarized Rayleigh scattering spectra of polypropylene glycol is due to backbone segmental motion.

The depolarized Rayleigh light scattering spectra of pure polyethylene glycols and their solutions in an optically isotropic solvent were also studied as a function of polymer molecular weight, concentration and temperature[10]. By studying the dependence of relaxation times on viscosity, temperature and concentration and comparing the results with theoretical predictions of molecular and end-group reorientations, it was concluded that the depolarized Rayleigh spectra of the low molecular weight oligomers of polyethylene glycol are associated with rotation of the entire polymer molecules.

Thus, it is clear that both the localized segmental motion and the overall molecular reorientation can contribute to the depolarized Rayleigh spectra of macromolecules in solution consisting of optically isotropic solvent. Using the experimental fact, we went on to study the problem theoretically[11,12] and from a general expression of the time-correlation function for polarizability, we have obtained naturally by the method of analysis two correlation functions respectively related to molecular rotation and local segmental motion. The future work would be to relate the dynamics involved in each type of the correlation function to the macroscopic properties of a polymer liquid which are easily measureable.

3) Polarized Raman Scattering Studies of Chain Orientation in Hydrostatically Extruded Polypropylenes.

As the extent of polymer-chain orientation is closely related to the mechanical and optical properties of a polymer, there is a considerable interest in determining the orientational state of the molecules in solid polymers. To demonstrate the effectiveness of the Raman scattering intensity measurement as a method for obtaining the information about orientational order parameter, the uniaxial hydrostatically extruded isotactic polypropylene has been investigated by polarized Raman scattering. By investigating the CH_2 twisting mode at 1256 cm^{-1}, quantitative results for the order parameter $<P_2(\cos\theta)>$ and $<P_4(\cos\theta)>$ have been obtained[3]. Functions $<P_2(\cos\theta)>$ and $<P_4(\cos\theta)>$ are the second and fourth moments of the orientational distribution function, where θ is the angle between the chain axis and the direction of extrusion. Alignment of polymer chains has been found to increase with increasing extrusion ratio. The measured $<P_2>$ values are found in good agreement with the birefringence data. Work of this kind is being continued for other solid polymers such as polyvinylidene chorolide and polyacrylnitrile.

III. Personnel Supported by the Office of Naval Research

The principal investigator completed work leading to referenced publications 1 through 13. Several graduate and postdoctoral students were supported during various phases of the Office of Naval Research project:

a) Graduate and Undergraduate Students

>   Mr. Scott P. Hunter
>
>   Mr. Leo Smith
>
>   Mr. C. Kit Cheung
>
>   Mr. Scott Whittenburg
>
>   Mr. Y.-H. Lin

b)   Postdoctoral Research Associates

Dr. Dane Jones

Dr. Sushil Satija

Dr. Y.-Y. Huang

Dr. Y.-Y. Huang initiated the project on polypropylene glycol before joining ITT Corporation in 1976. Mr. Scott Hunter and Dr. Dane Jones continued the projects after Dr. Huang had left. Mr. Leo Smith assisted in setting up equipment for polymer purification which was designed by Dr. Dane Jones. Mr. Kit Cheung carried out the Brillouin and depolarized Rayleigh measurements on polyoxymethylene ethers, which have not been published. Mr. Scott Whittenburg was responsible for automating the light scattering equipment in our laboratory as well as for setting up the photon correlation spectrometer. The photon correlator has been calibrated and is now ready for carrying out a research project. This equipment has extended our capability for investigating the dynamic process involved in the polarized Rayleigh scattering process. Mr. Y.-H. Lin was responsible for developing a generalized hydrodynamic theory to interpret the Brillouin scattering data. Mr. Lin left the University of Utah for a postdoctoral position at SUNY at Stonybrook after finishing his Ph.D. degree in June, 1978. Mr. Whittenburg is finishing in December, 1978 and will become an assistant professor at the University of New Orleans. Finally, Dr. Satija did the Raman scattering work on hydrostatically extruded polymers and is continuing on to other solid polymer systems using the same technique. The photon correlator built by Mr. Whittenburg will be inherited by Mr. Walter Lempert, who is a new graduate student, recently joining my laboratory.

IV. <u>Papers and Presentations Derived from the Office of Naval Research Project Work</u>

Papers are listed as ref. 1 through 13 in the reference section below. Stu-

dent thesis are listed as reference 16 and 17. Several talks and invited presentations at national and international meetings are listed below:

1) The Third International Conference on Light Scattering Solids, Compinas, Brazil, August, 1975, "Brillouin Scattering of Polymer Liquids."

2) Department Colloquium, Department of Chemistry, University of Colorado, April 1976, "Brillouin and Depolarized Rayleigh Scattering of Polypropylene Glycols."

3) Gordon Research Conference on Polymer Physics, New Hampshire, July, 1976, "Brillouin Scattering and Viscoelasticity of Liquid Polymers."

4) The Fifth International Conference on Raman Spectroscopy, Freiburg, West Germany, September, 1976,

5) Centre de Recherches sur les Macromolecules, Strasbourg, France, September, 1976, "Depolarized Rayleigh Scattering and Molecular Reorientation in Polyethylene Glycol."

6) ONR Contrators Meeting, U.S. Naval Academy, Annapolis, Maryland, June, 1977, "Brillouin and Rayleigh Scattering of Liquid Polymers."

7) ONR Contractors Meeting, The University of Massachusetts, Amherst, Massachusetts, October, 1977, "Brillouin Scattering and Chain Orientation in Hydrostatically Extruded Polyethylene."

8) Physical Chemistry Seminar, Department of Chemistry, University of Wisconsin, Madison, October, 1977, "Brillouin-Rayleigh Scattering and Segmental Motion of Polymers."

9) Department Colloquium, Department of Material Science, University of Utah, Salt Lake City, November, 1977, "The High Frequency Properties of Bulk Polymers as Investigated by Brillouin Spectroscopy."

10) Department of Physics Seminar, The University of Dortmund, Dortmund, West Germany, May, 1978, "Brillouin-Rayleigh Scattering of Viscoelastic Polymers."

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1. Y. Y. Huang and C. H. Wang, J. Chem. Phys. 61, 1868 (1974), "Brillouin and Rayleigh Scattering in Polybutadiene."

2. Y. Y. Huang and C. H. Wang, J. Chem. Phys. 62, 120 (1975), "Brillouin, Rayleigh and Depolarized Rayleigh Scattering Studies of Polypropylene Glycol. I."

3. C. H. Wang and Y. Y. Huang, *Light Scattering in Solids*, eds. M. Balkanski, R.C.C. Leite and S.P.S. Porto (Flomariam) Paris, pp. 732-736 (1975), "Brillouin and Depolarized Rayleigh Scattering of Light in Polypropylene Glycols. II."

4. C. H. Wang and Y. Y. Huang, J. Chem. Phys. 64, 4847 (1976), "Brillouin-Rayleigh Scattering Studies of Polypropylene Glycol. III."

5. S. Yano, R. R. Rahalkar, S. P. Hunter, C. H. Wang and R. H. Boyd, J. Poly. Phys. Ed. 14, 1877 (1976), "Studies of Molecular Relaxation of Poly(propylene Oxide) Solutions by Dielectric Relaxation and Brillouin Scattering."

6. Y.-H. Lin and C. H. Wang, J. Chem. Phys. 64, 1546 (1978), "Brillouin Scattering and Segmental Motion of a Polymeric Liquid. I."

7. Y.-H. Lin and C. H. Wang, Mole. Phys. (in press), "Brillouin Scattering and Segmental Motion of a Polymer Liquid. II."

8. Y.-H. Lin and C. H. Wang, J. Chem. Phys. (in press), "Rayleigh-Brillouin Scattering and Structural Relaxation of a Viscoelastic Liquid."

9. D. R. Jones and C. H. Wang, J. Chem. Phys. 65, 1835 (1976), "Depolarized Rayleigh Scattering and Backbone Motion of Polypropylene Glycol."

10. D. R. Jones and C. H. Wang, J. Chem. Phys. 66, 1659 (1977), "Depolarized Rayleigh Scattering and Orientational Motion of Polyethylene Glycol."

11. Y.-H. Lin and C. H. Wang, J. Chem. Phys. 66, 5578 (1977), "A Theoretical Study of the Depolarized Rayleigh Scattering Time-Correlation Function of a Dilute Polymer Solution."

12. C. H. Wang and Y.-H. Lin, J. Coll. and Interface Sci. 63, 270 (1977), "Depolarized Rayleigh Scattering of Dilute Polymer Solutions."

13. S. K. Satija and C. H. Wang, J. Chem. Phys. 69, 2739 (1978), "Polarized Raman Scattering Studies of Chain Orientation in Hydrostatically Extruded Polypropylene."

14. C. K. Cheung and C. H. Wang, (to be published), "Brillouin and Depolarized Rayleigh Scattering of Polyoxymethylene Ether."

15. W. Lempert and C. H. Wang, (to be published), "Brillouin Scattering of Polystyrene-Cyclohexane Solution."

16. Thesis; Yn-Hwang Lin, "Depolarized Rayleigh and Rayleigh-Brillouin Scattering Studies of Segmental Motions of Polymer Fluids", University of Utah, 1978.

17. Thesis; Scott L. Whittenburg, "Light Scattering Studies of Molecular Motion in Liquids", University of Utah, 1978.

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